“Exploring Dielectric Spectroscopy in some Polar Compounds using Time Domain Reflectometry"

Synopsis

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1. Introduction

Dielectric behavior is a widely studied phenomenon in materials science and chemistry, providing valuable insights into the intermolecular interactions and dynamics of molecules in a bulk medium. In this context, the investigation of mixtures plays a crucial role as it allows for a deeper understanding of the behaviors and interactions between different constituents of particular interest in the study of mixtures of substituted anilines and alcohols [1-10]. Where substituted anilines represent a prototypical aromatic amine, and alcohols serve as a commonly used solvent. Notably, these mixtures exhibit intriguing dielectric properties due to the unique nature of their molecular structures and the potential for hydrogen bonding interactions. Time Domain Reflectometry (TDR) stands out as a powerful technique for exploring the dielectric properties and relaxation mechanisms in these mixtures. TDR is a non-destructive, non-invasive method that measures the complex permittivity of a sample as a function of frequency and temperature. It provides valuable information on the molecular dynamics, polarization processes, and relaxation timescales of the sample under investigation. The dielectric study of binary mixtures of substituted anilines and alcohols using TDR serves as a valuable platform to gain insights into the influence of various molecular parameters, such as composition, temperature, and molecular structure on the dielectric behavior [11-16]. The presence of amine groups in the mixture of substituted anilines and alcohols plays a significant role in the dielectric properties and relaxation dynamics. The amine group contains a lone pair of electrons, making it highly polarizable and capable of forming hydrogen bonds with neighboring molecules. The concentration of amine groups in the solution can modulate the dielectric properties due to the changes in molecular interactions. Higher concentrations of amine groups can enhance the degree of hydrogen bonding and lead to pronounced changes in dielectric behavior, including shifts in relaxation frequencies and changes in relaxation strengths
[17-24]. Temperature has a crucial role in the dielectric study of mixtures containing amine groups. As temperature increases, the strength of hydrogen bonding decreases, resulting in the alteration of relaxation timescales and dielectric properties.

The aim of the present work is devoted to the study of dielectric parameters providing a comprehensive overview of the experimental techniques, theoretical models, material science, solvent characterization and research methodologies employed to investigate the dielectric parameters.

2. Review of literature and development in the subject

The interaction between anilines and alcohols is a subject of interest in the field of chemistry, especially in the context of solvent-solute interactions, solution behavior, and related applications. Here are some aspects of the interactions between anilines and alcohols**.** In 2015, Kemeakegha et al.[25] studied the volumetric behavior at 298.15 K for mixtures of 2-methoxy ethanol and 2-ethoxy ethanol withdiethylamine, triethylamine, tert-butylamine, hexylamine, benzylamine and aniline. Excess molar volume was evaluated using the density data. The calculated excess molar volume was fitted into the Redlich-Kister polynomial equation to obtain fitting coefficients and standard deviations. Excess molar volume for studied mixtures was found to vary in negatively indicating the formation of strong interactions. In 2017, Alisha et al. [26] reported the ultrasonic behavior of binary mixtures of triethyl-amine with 2-(2-methoxy-ethoxy) ethanol, 2-(2-ethoxy-

ethoxy) ethanol and 2-(2-butoxy-ethoxy) ethanol at 308.15 K. Parameters like isentropic compressibility, acoustic impedance and intermolecular free length were computed. Using these parameters various excess properties were computed. Trends in the variation of these parameters suggested the presence of strong molecular interactions among components. With the increase in the alkoxy group in 2-(2-alkoxyethoxy) ethanol molecules, interactions were found to increase. Volumetric and acoustic behavior for binary mixtures of di-n-butylamine with 1-propanol, 2-propanol, 1-butanol and 2-butanol was studied by Dubey et al.[27].At different temperatures in 2017. Excess molar volume, excess molar isentropic compressibility, deviation in speed of sound and excess Gibbs free energy have been evaluated using the experimental data. Strong interactions among unlike molecules in the mixture were confirmed by these parameters. PFP theory was used for the estimation of excess molar volume values. Dubey and Kaur [28] have measured the density and ultrasonic speed for mixtures of 2-isopropoxy ethanol with 1-hexanol, 1-octanol and 1-decanol at 293.15-313.15 K and viscosity at 298.15-308.15 K in the same year. Weak interaction among unlike molecules was revealed by parameters calculated using the experimental data. Interactions were found to decrease with an increase in the size of alcohol molecules. FTIR and NMR studies for these mixtures were also carried out. Three parameters of semi-empirical relations of viscosity namely Heric-Brewer and McAllister were also tested.Dubey et al.[29] have reported the volumetric and acoustic behavior for binary mixtures of di-n-butylamine and di-iso-propyl-amine with 2-butanol and 2-pentanol at temperatures 293.15, 298.15, 303.15 and 308.15 K in 2019. Excess molar volume, excess molar isentropic compressibility, deviation in the speed of sound, excess intermolecular free length, excess acoustic impedance, excess partial molar volume and apparent molar volume have been evaluated using the experimental data. Strong interactions among components were confirmed by these parameters. Interactions were found to be more in mixtures of di-is-opropyl-amine compared to mixtures of di-n-butylamine. FTIR study of binary mixtures was also carried out.M. V. Alexander and G. Meenakshi [30] studied the acoustic behaviorof a mixture of hexane-1-ol with N,N-di-ethyl-ethane-amine in cyclohexane medium at 303 K and 308 K in 2021. Various acoustic parameters were computed using the measured data and discussed in terms of molecular interactions.
Research in this area continues to explore the nuances of these interactions, and ongoing studies contribute to a deeper understanding of the molecular behavior of anilines and alcohols in different contexts.

3. Objective of research/Proposed Hypothesis:

The plan is to carry out high-frequency dielectric measurements of amine solutions with solvent using time domain dielectric relaxation spectroscopy technique having a frequency range of 10MHz to 50GHz at different temperatures. Therefore, the present objective of the work is to study the solute &solvent molecules and determine the **complex permittivity** of amines in solvents using Time Domain Reflectometry Technique from 10 MHz to 50 GHz. To determine **static dielectric constant, dielectric loss and relaxation time** at high frequency. To study molecular interaction and hydrogen bonding of solvents through various parameters like **Krikwood correlation factor, Bruggman factor, Thermodynamic Parameters and Excess parameters** etc. using picoseconds dielectric-relaxation spectroscopy.

4. Methodology to be adopted

In our quest for knowledge, a meticulous methodology shall serve as our compass. With precision akin to an artisan's craft, we shall employ the following steps to unravel the complex dielectric spectra through the venerable Time Domain Reflectometry (TDR) technique. **Experimental Setup.** Our journey commences with the Tektronix model no. DSA8300 Digital Serial Analyzer, a paragon of precision and its accompanying sampling module. This tandem shall wield the powers of Time Domain Reflectometry. Behold Figure 1, which unveils the experimental setup a testament to our scientific endeavor [31]. **Pulse Generation.** In the heart of our experiment lies a rhythmic heartbeat a repetitive, fast-rising 250mV voltage pulse and a symphony resonating at 200 KHz. Its pulse has a swift 12ps incident and a reflective rise time of 15ps. It courses through a coaxial line system with an impedance of 50 ohms, a conductor of our inquiries [32]. **Sampling Oscilloscope.** As our pulse travels, the vigilant eye of a sampling oscilloscope stands sentinel. It captures the metamorphosis of the pulse as it reflects from the end of its journey. The reflected pulses naked and veiled by the sample bear witness to our experiment. A 5 ns time window is their canvas and they are painted in the strokes of 2000 points as depicted in Figure 2. **Data Manipulation.** The pulses dance in pairs one from the pristine reflection (R1(t)) and the other entwined with the essence of the sample (Rx(t)). They are summoned forth, both in their original form [q(t)=R1(t) + RX(t)] and in their contrast [p(t) =R1(t)-RX(t)]. These forms reveal the essence of our investigation [33]. **Transformation into the Frequency Domain.** With the data in hand, we embark on a voyage from the time domain into the realm of frequencies. In the Fourier transformation, a magician's incantation shall conjure the spectral secrets hidden within. Summation and Samulon methods shall be our loyal companions in this endeavor. Our goal is to reach frequencies up to 50GHz and therein to uncover the frequency-dependent complex reflection coefficient spectra, $\rho^*(\omega)$, as per [34].

$$(\rho)^*= c \quad p(\omega)/ j\,\omega d\, q(\omega) \qquad (1)$$

where c is the velocity of light in mm/ps, ω is the angular frequency and d is the effective pin length. The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from complex reflection spectra $\rho^*(\omega)$ by using bilinear calibration method given by

The Quest for Complex Permittivity: The elusive complex permittivity spectra $\varepsilon^*(\omega)$, await our discovery. From the complex reflection spectra $\rho^*(\omega)$ we shall extract this enigma using the bilinear calibration method a method encapsulated by the equation [35].

$$\varepsilon^*(\omega)=\varepsilon_{\infty+}(\varepsilon_0-\varepsilon_\infty)/\,[(1+(j\omega\tau)^{1-\alpha}]^{\beta} \quad (2)$$

Here, ε_0 stands as the static dielectric constant, ε represents the permittivity at high frequency, τ is the relaxation time, while α and β embody the symphony of symmetric and asymmetric distribution of relaxation times, respectively. Behold the Havriliak-Negami equation a portal into the mysteries of three relaxation models, each with its unique character:

1. If $\alpha = 0$ and $\beta = 1$, we embrace the simplicity of a single Debye relaxation.
2. When $0 \leq \alpha \leq 1$, we traverse the labyrinth of the Cole-Cole model with a symmetric distribution of relaxation times.
3. And when $\alpha = 0$, while β ranges from 0 to 1 we encounter the enigmatic Cole-Davidson (CD) an asymmetric distribution of relaxation times.

With these meticulous steps and the symphony of our instrumentation, we embark on a journey to reveal the hidden facets of complex dielectric spectra an odyssey that shall enlighten the corridors of scientific understanding.

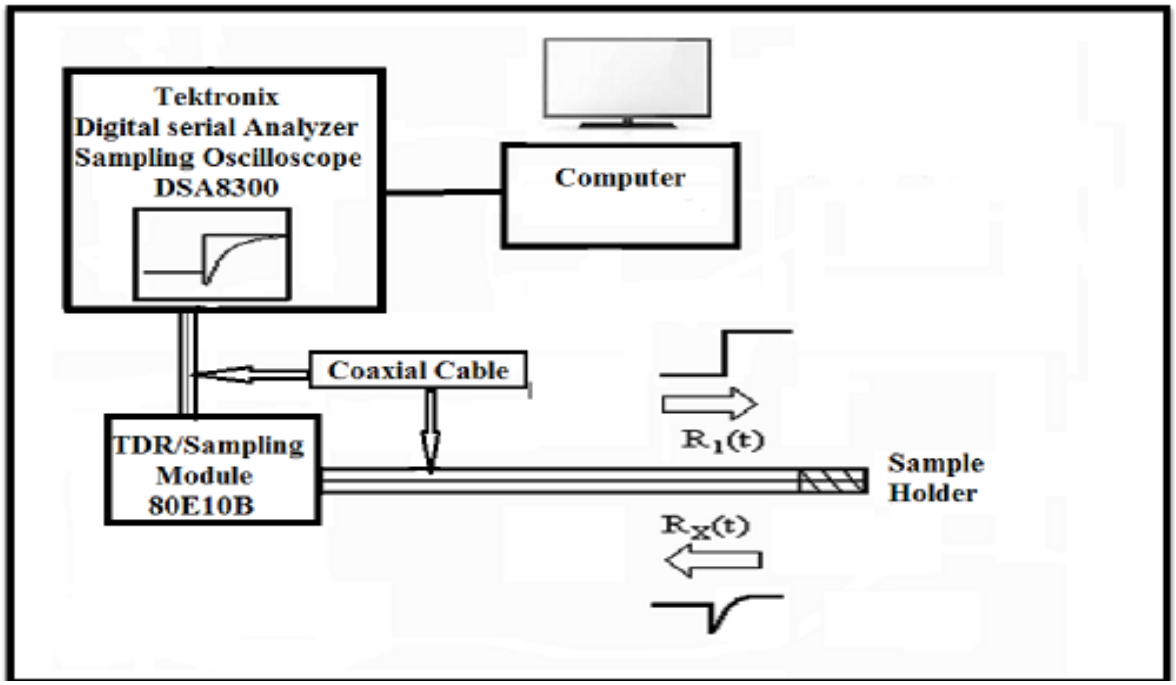

Fig. (a)

Fig1. (a)Block diagram of Time Domain Reflectometry. (b) Photograph of TDR

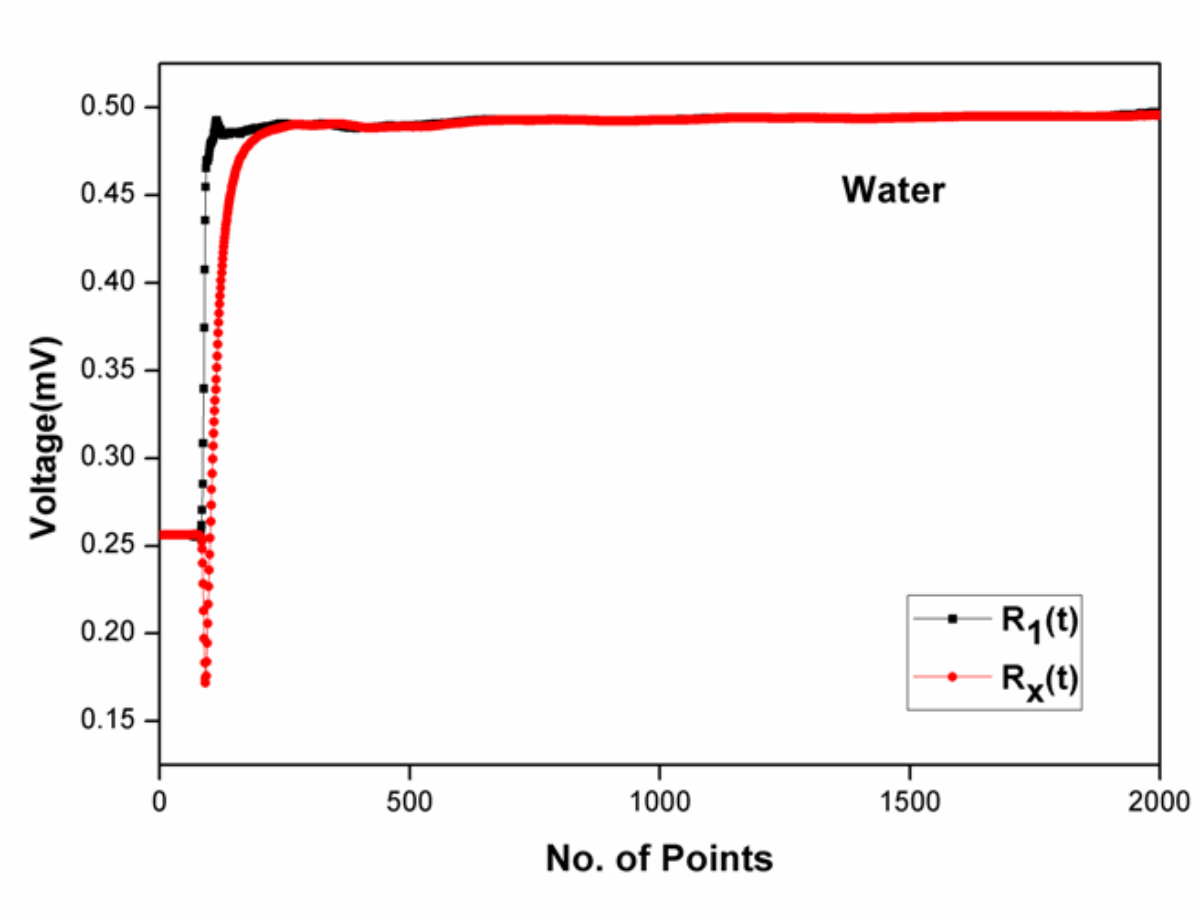

Fig.2 Reflected pulse without sample *R1(t)* & sample *Rx(t)*.

5. Importance of Study / Society application

The study of the interaction between substituted anilines and alcohols is significant for various reasons, including its potential applications in society. Here are some key points highlighting the importance of this study. Aniline and its halogenated derivatives in combination with alkoxyalcohol have diverse applications across several industries due to their unique properties. Some of these applications include. **Herbicides and Pesticides**, some halogenated aniline derivatives possess pesticidal properties and are used in the production of herbicides and pesticides to control pests or unwanted vegetation. **Electronics,** aniline derivatives are employed in the manufacture of conducting polymers used in electronic devices. The introduction of halogenated groups can alter their electrical conductivity or other electronic properties. Alkoxyalcohol might serve as solvents or additives in electronic material fabrication. **Photography**, aniline derivatives have historical usage in the production of photographic chemicals. Halogenated derivatives might exhibit specific light-sensitive properties beneficial in certain photographic applications. **Chemical Intermediates**, aniline, and its derivatives, including halogenated variations, are vital intermediates in synthesizing various chemicals and compounds, finding application in diverse chemical processes across industries.

These applications highlight the versatility and significance of aniline derivatives, including halogenated variations, along with alkoxyethanols in various industrial sectors. Their specific properties, reactivity, and functionalities make them valuable in different processes and product formulations.

6. International status/National status:

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7. Proposed work plan

Your proposed work plan for a three-year research project on dielectric measurements of haloanilines and substituted alcohols seems well-structured. Here's a breakdown of the plan.

First Year: Literature Survey and Solvent Selection

- **Objective:** To build a strong foundation for our research and select appropriate solvents for our
- experiments.
- **Activities:**
  - Conduct an extensive literature survey to understand the existing knowledge in the field.
  - Identify key research gaps and areas where your study can contribute.
  - Familiarize yourself with dielectric measurement techniques and equipment.
  - Begin the process of solvent selection, considering factors like solubility, stability, and relevance to our research.

Second Year: Dielectric Measurements

- **Objective:** To conduct dielectric measurements on haloanilines with substituted alcohols and extract essential dielectric parameters.
- **Activities:**
    - Acquire and set up the necessary equipment for dielectric measurements.
    - Prepare samples of amines in various solvents as per your solvent selection criteria.
    - Perform dielectric measurements at different frequencies.
    - Extract dielectric parameters, including static dielectric constant, relaxation time, dielectric constant at high frequency, and Kirkwood correlation factor.

Third Year: Dielectric and Structural Behavior Study

- **Objective:** To delve deeper into the dielectric and structural behavior of haloanilines with substituted alcohols by analyzing dielectric relaxation parameters.
- **Activities:**
    - Analyze the data collected from dielectric measurements.
    - Study how dielectric parameters vary with changes in concentration, temperature, or other relevant factors.
    - Investigate the structural aspects and molecular interactions within the solutions.
    - Determine any correlations or trends between dielectric behavior and the molecular structure of the haloanilines with substituted alcohols.
    - Summarize our findings and conclude the dielectric and structural behavior of haloanilines in substituted alcohols.

Throughout the three years, it's crucial to maintain meticulous records of our experiments, data analysis, and observations. Additionally, consider incorporating regular progress assessments, presentations, and discussions with your research advisor or team to ensure that our research stays on track and aligns with our objectives.This work plan provides a solid framework for our research project, allowing me to systematically explore the dielectric behavior of amines in various solvents and contribute valuable insights to the field.

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